REFRACTORIES FOR GLASS PRODUCTION

SERVICE SPECIFICS OF REFRACTORY LINING IN A FLOAT TANK AND TESTS OF NEW HEAT-RESISTANT COMPOSITE MATERIALS

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To avoid glass defects as a consequence of lining destruction in service and to preserve the operating conditions of a float tank equipment, it is necessary to use high-quality refractory materials which are developed taking into account their service specifics. Researchers at the Saratov Institute of Glass have identified maximum admissible fluctuation parameters for the gaseous atmosphere composition in the metal tank, which influences the destruction of refractory lining. New types of composites, namely, concretes on a refractory chamotte basis produced at the Semiluki Refractory Works, have been tested in the service conditions.

A tank filled with tin melt is the main technological unit of the float-glass process in which fire-polished glass surface is produced. The state of equipment and the proper melt tank (a sealed metal tank lined with a refractory) determine mainly the quality of the glass surface. In order to prevent numerous possible glass defects caused by the lining that can be destroyed in service, decrease the consumption of expensive tin (to decrease impregnation of refractories with tin), and extend as much as possible the working state of the melt tank equipment, the refractory lining should be produced from the most suitable high-quality material. The selection and development of corresponding materials are possible only taking into account the service specifics of refractories in a float tank, which do not exist in other production processes. The principle of the formation of a polished glass ribbon on the surface of metallic melt involves using tin. Such properties of tin as its melting and boiling temperature and vapor pressure make it possible to use it in the liquid state without significant evaporation in the temperature range of glass formation (1050 – 600°C).

Glass melt arriving at the tin melt tank is supersaturated with various gaseous compounds, including oxygen-bearing ones, and is a far-from-equilibrium system which permanently generates oxygen compounds reacting with tin and refractories. Tin inevitably becomes oxidized in the presence of oxygen and water vapor. The product of oxidation is SnO_2 with SnO impurity. Tin dioxide tends to be formed from the tin melt in the "cold" end of the tank, where the temperature is equal to 560 – 590°C. These compounds are formed as solid films on the melt surface and stick to the bottom surface of the glass, while their vapor is condensed on the refractory roof and on the coolers and deposited on the upper surface of glass in the forms of drops. This inflicts irreparable damage on the glass.

Consequently, all physicochemical parameters of the glass-forming process are directed both to the development of a polished surface of the glass ribbon and preventing the formation of tin oxides. Since the penetration of oxygen and oxygen-bearing compounds into the melt tank is inevitable, their continuous removal from tin and from the gaseous space of the melt tank is provided by supplying a reducing nitrogen-hydrogen atmosphere of a high degree of purity. The presence of active hydrogen in the float-tank atmosphere at a high temperature and its intense effect on the tin melt facilitates various interactions in the multicomponent system "glass – tin – protective atmosphere – refractory."

The maximum thermodynamic probability of tin reduction exists at high temperatures. At the tin melt temperature of 600 – 630°C, the thermodynamic probability of tin oxide reduction in the "cold" end of the tank is virtually absent [1]. In practice, such difficulties are overcome by various methods that accelerate the reactions of tin oxide reduction. Such a method for the tin melt tank raises the concentration of the reducing agent (hydrogen). Its effect is explained by the concept of the equilibrium constant, which is equal to the ratio of the pressure of the vapor of the gaseous reaction products (in this case water) to the pressure of the vapor of the initial reactants (hydrogen) upon achieving their equilibrium for the particular temperature [1].

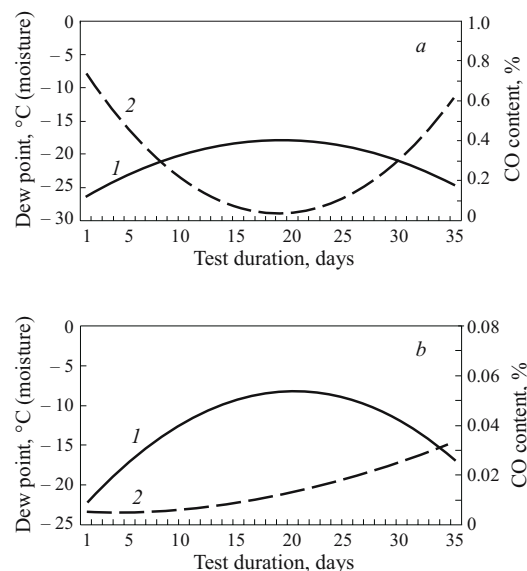[1] Saratov Institute of Glass, Saratov, Russia; Semiluki Refractory Works, Semiluki, Russia.

Fig. 1. Variations in CO and moisture content in gaseous atmosphere at testing temperatures of 600°C (*a*) and 1000°C (*b*) of samples fired at 380 and 1000°C: *1*) dew point (moisture); *2*) CO content.

TABLE 1

Conditions of testing samples		Sample characteristics	
installation site and temperature	maximum CO content, %	heat treatment, °C	strength after testing, N/mm²
Gaseous atmosphere, 1000°C	0.01 – 0.07	400	32.24 – 48.52
	0.01 – 0.07	1000	49.70
	0.05	1000	40.27
	0.20 – 0.27	1400	61.09
Contact with tin, gaseous atmosphere, 600°C	0.40 – 0.88	400	40.50 – 53.40
	0.40 – 0.88	1000	External damage
	The same	1000	43.05
	The same	1400	57.37

refractories being destroyed under an increased concentration of CO [3].

To determine the maximum admissible parameters of fluctuations in the gas medium composition in the melt tank with respect to carbon oxide content, which causes destruction of refractory lining, researchers at the Saratov Instate of Glass have tested refractory samples in service conditions. We have tested new types of composite materials: concretes based on refractory chamotte supplied by the Semiluki Refractory Works. Cube-shaped samples were subjected to preliminary heat treatment (up to 400°C) at the manufacturer's factory. Some of them were subjected to additional firing to the maximal temperatures of 1000 and 1400°C in the oxidizing conditions of a gas-flame furnace. The samples were placed in different temperature and gas-variable conditions. Some of the samples at the temperature 550 – 600°C found at the exit end of the melt tank were introduced into a protective nitrogen-oxygen gaseous atmosphere on the surface of the tin melt where they became partly immersed in the melt. Tests of samples immersed in the tin at 600°C established that concrete samples that had been prefired to the maximal temperature of 1000°C in a gas-flame furnace showed visible destruction with a weight loss up to 20%. Destruction occurred in the upper part of the sample surrounded by the gaseous space containing an increased content of carbon oxide. Samples of the same material that had been heat-treated at 400°C and tested at the same time did not exhibit signs of destruction. The samples placed in high-temperature conditions (around 1000°C) with a different composition of the gaseous medium, as well as samples contacting tin melt, showed no signs of destruction.

Microscopic study of the destroyed samples identified traces of a carbonaceous material. The variations in the gaseous medium parameters, i.e., the content of CO and moisture (dew point) during the experiment, are shown in Fig. 1. It should be noted that the testing temperature was maintained rather steady, within admissible limits.

The criteria for identifying a negative effect of service factors were external damage and a decrease in mechanical strength of the samples. The compressive strength of samples and the content of CO in the protective gas atmosphere are listed in Table 1.

In reality, the reduction conditions are far from equilibrium. However, as water vapor is continuously removed from the reaction zones, the hydrogen vapor pressure tends to decrease, which is possible only due to its accelerated flow rate for the reduction reactions. Hence the requirement for maintaining a higher concentration of hydrogen in the low-temperature zone of the melt tank, whereas the moisture content in the supplied gas is set at a minimum level, and the high multiplicity of renewal of the protective atmosphere in the tank is maintained as well.

In practice, an increased moisture content in the gas-protective atmosphere of the melt tank under a constant quantity of hydrogen supplied may be an indication of oxygen penetrating into the tank. Vice versa, a reverse course of the reactions and the formation of tin oxides become possible under a significant excess of water vapor pressure over hydrogen vapor pressure. The damaging effect of water vapor is related to its reaction with tin and saturating tin with dissolved oxygen. Since oxygen is a surfactant, it is adsorbed on the tin surface and decreases its interphase surface tension; as a consequence, the ability of tin to wet glass and refractories grows and the formation of crystalline tin oxides increases [2].

Thus, all components of the gaseous medium in a melt tank actively interact and the course of the reaction depends on the stability of the parameters of constantly maintained reducing conditions.

There is an opinion that carbon monoxide, which is a commonly available intense reducing material, can be used in the atmosphere of the melt tank as the reducing agent. Furthermore, a certain quantity of CO may be present in the gaseous atmosphere of the melt tank in using a protective mixture based on natural gas and in making decorative glass. However, industrial practice reports examples of chamotte

During the experiment when the samples fired at 1000°C were destroyed at the temperature of 600°C, the content of CO in the gaseous atmosphere grew to 0.40 – 0.88% and remained high for a long time. Under testing in high-temperature conditions (1000°C) the content of CO in the protective gaseous atmosphere was significantly lower and amounted to 0 – 0.01% with occasional peaks to 0.06 – 0.07%.

In repeated testing at 600°C of concrete samples fired up to a temperature of 1000°C, CO was absent from the atmosphere; under the maximum testing temperature up to 1000°C its content did not exceed 0.05%. Subsequent compressive strength testing demonstrated high strength of samples that had been treated in the absence or with a small quantity of CO (not more than 0.05%, with a single peak to 0.20 – 0.25%). As the samples prefired up to 1400°C were tested in high-temperature conditions (up to 1000°C), the content of CO grew to 0.20 – 0.27% for a short time. No visible changes were observed in the state of the samples.

The above data show a loss of strength in refractory materials under a protracted increased content of CO in the gaseous atmosphere.

The mechanism of destruction of concrete samples under an increased concentration of carbon monoxide appears as follows. When carbon monoxide penetrates into a mixture of hydrogen with nitrogen, it leads to an inevitable formation of soot, carbon dioxide, and moisture, whose quantity for each temperature depends on reaching a respective equilibrium during the respective reactions:

$$2CO = C_{sol} + CO_2 \text{ (Bel reaction)};$$

$$H_2 + CO_2 = H_2O + CO.$$
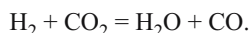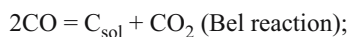
The soot becomes deposited on glass and refractory lining. The temperature range of formation of soot carbon formed according to the Bel reaction is 450 – 600°C, i.e., these are precisely the conditions in the "cold" zone of the melt tank. The reaction of the formation of soot carbon occurs inside the porous body and is accelerated by the catalysts represented by metallic iron [3]. Soot carbon itself is not the reason for the destruction of refractories. The destruction is caused by the reduction (at relatively low temperatures) of iron oxides to metallic iron and the interaction of metallic iron with carbon monoxide leading to the formation of carbides and oxides. The emerging metallic iron has a well extended surface and a defective crystal lattice. In the case of reduction of iron oxides in the free state at a temperature above 572°C, the reactions occur in the following order:

$$Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO \rightarrow Fe.$$
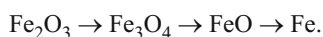
These reactions proceed with a substantial volume expansion due to the formation of carbide and oxides as a consequence of reactions with CO. The calculated volumetric effect of these reactions is listed below [3]:

Final product	Volumetric reaction effect
Fe_3C	+ 10
FeO	+ 78
Fe_3O_4	+ 109

The increased volume causes stresses in the bodies of refractories exceeding their strength and leading to their destruction. Apart from the Bel reaction, soot carbon is formed as well according to the following reaction:

$$CO + H_2 \leftrightarrows C + H_2O.$$
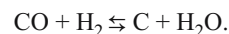
The increasing content of moisture in the gaseous atmosphere, as the concentration of carbon monoxide decreases, supports this assumption (Fig. 1). Water vapor as well can reduce iron to Fe^{3+}. Methane, natural gas, ethane, and other hydrocarbons are capable of releasing soot carbon in the presence of catalysts. They have a wider range of active temperatures for soot carbon formation than carbon monoxide, which is related to their decomposition temperatures. Since the reaction of formation of soot carbon is catalyzed, it is interesting to carry out studies directed to delaying the formation of soot carbon.

Furthermore, the tested samples of composite concrete provided by the Semiluki Refractory Works after preliminary heat treatment at a temperature at least 400°C and without additional firing in a gas furnace were not destroyed in the atmosphere with an increased CO content, most probably due to the absence of a substantial quantity of open pores, which are formed on the surface of refractories under high-temperature firing.

The performed tests suggest as well that the preferred material for the float tank lining is the unfired concrete composite based on refractory chamotte, whose structure subsequently evolves under the effect of service factors and is the most adequate to the melt tank conditions.

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